A Study of the Effect of Certain Electrolytes on Stabilizing and Precipitating Gold Sols.

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY

BY

DAVID J. BEAVER, B.S., M.A.

NEW YORK CITY

1921

The Jackson Press, Kingston
1921

TO

PROFESSOR FRANK S. HOFFMAN

ACKNOWLEDGMENT

The author wishes to express to Professor H. T. Beans his sincere thanks for the suggestion of the problem, and for his generous assistance and advice throughout the course of the investigation.

He also wishes to thank the other members of the Chemistry Department for their co-operation and assistance.

Digitized by the Internet Archive
in 2025

https://archive.org/details/studyofeffectofc0000davi

A STUDY OF THE EFFECT OF CERTAIN ELECTROLYTES ON STABILIZING AND PRECIPITATING GOLD SOLS

The fact that certain colloidal dispersions were stable only in the presence of small amounts of electroytes was first observed by Graham[1], who found that ferric hydroxide and aluminum hydroxide sols could not be entirely freed from chloride, no matter how long the solutions were dialysized. Neidle[2] showed that the stability of ferric hydroxide sols increased with the amount of chloride ion present, (within certain limits), while Young and Goddard[3] found that the dispersive effect of hydrogen sulphide on zinc sulphide increased with pressure of the hydrogen sulphide, and that it had a protective effect in the precipitation of this sulphide by potassium chloride. A great deal of similar work has been done with other hydrosols showing that the presence of electrolytes is necessary to stabilize the colloid.[4] The application of this so-called "complex" theory of colloids was limited to emulsoids (lyophilic dispersions) since it was thought that suspensoids (lyophobic dispersions), particularly those of the noble metals prepared by electrical dispersion, were stable in pure water.[5] Bredig[6], however, recommended the use of 0.001N sodium hydroxide, while Whitney and Blake[7] claimed that "a more stable and more concentrated sol could be obtained by sparking gold electrodes in the presence of a solution of hydrochloric acid having a conductivity of 200 x 10^{-6} mhos." In the paper of Beans and Eastlack[1] it was shown that gold sols prepared by electrical dispersion could be stabilized only by electrolytes in concentrations between 0.005N and 0.00005N, which have a negative ion able to form stable compounds with gold. The object of the present work is to try to find an explanation of the mechanism of: 1st, the stabilizing action of certain electrolytes on

[1]Chem. and Physical Researches, pp. 582, 580 (1876).
[2]J. A. C. S. 39, 2334 (1917).
[3]Jour. Phy. Chem. 21, 1 (1917).
[4]For a summary of this work see Cassuto, Der Kolloide Zustand der Materie (1913), pp. 190-214.
[5]Freundlich, Kapillarchemie (1909), pp. 323-4; Cassuto, p. 213; and Taylor, The Chemistry of Colloids (1915), p. 110.
[6]"Anorganische Fermente," Dissertation, Leipzig (1901), p. 26.
[7]J. A. C. S. 26, 1376 (1904).
[1]J. A. C. S. 37, 2667 (1915).

gold sols prepared by electrical dispersion, and, 2nd, the precipitation of the stable sols by freezing and by centrifuging.

In the first place it is evident that if certain negative ions form "complexes" with the colloidal gold that they will no longer give their characteristic reactions in solution. The previous work of Beans and Eastlack[2] has shown that when the sol is precipitated by concentrated hydrochloric acid, the complex is most likely destroyed since there was no gold in the filtrate from the precipitated sols. Therefore in order to find the amount of the ion in this complex, it is necessary to be able to measure its concentration in solutions which contain it both as free ion and in combination with the gold. In order to do this, the measurements must be made in stable gold sols without precipitating the gold. There are two methods of measuring the concentration of ions in solutions which can be used in the presence of colloidal gold. The first one is the measurement of the hydrogen ion concentration of the solution by means of the hydrogen electrode, and the second one is to determine the change in conductivity of a solution while adding an electrolyte which has one ion which will form a difficultly soluble or a practically unionized compound with one of the ions already in solution. Because the first method is limited in its application to solutions in which there is a change in the hydrogen ion concentration of the solution, the measurement of the change in conductivity of solutions was used in the present investigation. Dutoit[1] showed that any two solutions could be titrated by means of conductivity curves provided they formed difficultly soluble or a practically unionized compound. Kolthoff[2] corroborated Dutoit's results in neutralization analysis, and further refined the method for use in titrating a weak acid with a weak base.

In the second place in order to find an explanation of the mechanism of the precipitation of the stable gold sols it is necessary that the precipitation be made without altering the amount of electrolyte present in the sols. The first method which was thought of as fulfilling these conditions was that of precipitating the sol by mechanical means. A centrifuge capable of developing a force 1200 times gravity was found to give a sol of constant gold content after one hour centrifuging,

[2]Loc. cit.
[1]J. Chem. Phy. 8, 27 (1910).
[2]Z. anorg. allgem. Chem. 111, 1 (1920).

which shows that this force is inadequate to precipitate the colloidal particles. Next a centrifuge developing a force 40,000 times gravity was used, and it was found that all stable gold sols could be precipitated in three minutes by this method without in any way altering the concentration of electrolyte present. The second method which fulfils the necessary conditions is the one of Zsigmondy[3], who found that all metal hydrosols could be completely precipitated by freezing the solution without changing the amount of the electrolytes present. Conductivity titration curves were made on sols after precipitation by these two methods, and the results so obtained were compared with the results obtained with stable sols by the same procedure. In this way an idea of the mechanism of the precipitation of the sols was obtained.

Apparatus and Materials Used.

All standard solutions were made up in water having a specific conductivity between 1 and 2 x 10^{-6} mhos. The hydrochloric acid was Baker and Adamson's c. p. acid; the potassium chloride was re-crystallized twice from conductivity water, fused in a platinum dish, powdered in an agate mortar, and kept in a desiccator over concentrated sulphuric acid; the silver nitrate was re-crystallized once from conductivity water and dried over concentrated sulphuric acid in a desiccator; the sodium hydroxide was made by filtering a saturated aqueous solution of the base through a dry filter paper, which separated all the carbonate and chloride. A weighed amount of this purified solution was diluted to the required volume with conductivity water. The sodium hydroxide solution was standardized against weighed amounts of Bureau of Standards pure benzoic acid and the hydrochloric acid standardized against the sodium hydroxide.

All measurements were made at 25° C. in a large electrically heated Freas thermostat which was regulated at 25° ± .003° C.

The gold wire and arcing apparatus was the same as that used by Beans and Eastlack[1], with the addition of a stirring device which was used only when concentrated sols were prepared.

[3]Kolloidchemie, p. 66 (1912).
[1]Loc. cit., p. 2673.

The centrifuge used for freeing the sols of coarse particles only was a "type 3 centrifuge" of the International Equipment Co., with rotating arms 2 feet in diameter and with a speed of 2000 r. p. m. This machine developed a force approximately 1200 times gravity. The centrifuge used to precipitate the sols was a "Sharples laboratory super-centrifuge" with a gold-plated inner bowl of 50 c. c. capacity. It was non-continuous in operation and capable of developing a force 40,000 times that of gravity.

Conductivity measuring set. The source of current was a small Vreeland oscillator, built to give frequencies of either 500 or 1000 cycles per second. All measurements were made with the higher frequency. The bridge was a Kohlrausch circular slide wire with extension coils. The resistance boxes were in two parts, the smaller one for use up to 1000 ohms had three dials and bifilar wound coils, while the larger one for use up to 110,000 ohms had two dials with Curtis coils. Two variable rotary air condensers of 0.0004 and 0.0025 micro-farad capacity were used in parallel with the resistance boxes to balance the capacity of the cell. For conductivity water and dilute solutions a cell of the type described by Beans and Eastlack[1], with a cell constant of 0.009512, was used, while for more concentrated solutions two cells of the Freas type with cell constants of 0.3458 and 0.3261 were used.

Criticism of Previous Work.

The first attempt at measuring the amount of electrolyte combined with colloidal gold was an indirect method described by Whitney and Blake[2], whose primary purpose was to measure the velocity of migration of gold particles. They measured the specific conductivity of their solutions before each migration against gold-beaters skin, siphoned off the clear water above the red precipitate of colloidal gold, added conductivity water to replace the water siphoned off, re-dissolved the red precipitate in this water by shaking, and then determined the conductivity of the resulting solution. They found that after each migration the conductivity decreased. They explained the decrease in conductivity on the assumption that the gold particles have chloride ions associated with them, and in each

[1]Loc. cit., p. 2674.
[2]J. A. C. S. 26, 1339 (1904).

successive migration some of these ions are lost. But according to their statement the decrease in the amount of chloride ions in the solution did not cause a "noticeable decrease in the amount of gold in solution." Their conclusion from these results is that the conductivity of the sol is due to the negative ions associated with the gold particles, but that these ions are not necessary to keep the sol stable. The following experiment is typical of the way sols prepared by electrical dispersion in electrolytes of varying concentrations acted when migrated in a tube similar to the one used in Whitney and Blake's work. The electrolytes used were hydrochloric acid, sodium hydroxide, and potassium chloride.

Sol prepared in 0.0005N HCl (0.4500 grs. of gold per liter).

	Specific Conductivity x 10^{-6} mhos.	Conductivity of water surrounding anode x 10^{-6} mhos.
1. Sol before 1st migration	189.9	3.949
2. Aqueous layer after 1st migration	10.13	240.8
3. Sol before 2nd migration (the water used had a conductivity of 1.949)	16.46	3.949
4. Aqueous layer after 2nd migration	3.744	122.9
5. Sol before 3rd migration	3.962	3.306
6. Aqueous layer after 3rd migration	2.052	21.91

The sol turned blue during the third migration, and would not travel with the current against gravity when diluted with water a fourth time. The blue particles settled quite rapidly when there was no current on. With a sol prepared in 0.001N hydrochloric acid it took four migrations to free the solution of enough chloride ions to cause the sol to precipitate. The invariable result, no matter what the concentration of the electrolyte was at the start, was to precipitate the sol when the concentration of the electrolyte had been reduced to a value between 0.00005N and 0.00001N. These results show that an electrolyte is necessary for the stability of the gold dispersion, but they do not give an explanation of the mechanism of the stabilizing action. They also contradict those of Whitney and Blake, and it seems necessary to account for these differences in some manner not included in their explanation. One possibility which presented itself was the presence of some protective colloid in the sols prepared by Whitney and Blake. In order to test this hypothesis a gold sol containing 0.01% gela-

tin was prepared. On migrating sols containing this amount of gelatin it was found that a red precipitate was deposited on the membrane next to the anode which did not change to blue even after four migrations. This red precipitate could be again dispersed in water by shaking, forming stable red sols.

The second method of measuring the amount of electrolyte combined with the colloidal gold was that of Burton[1], who measured the change in speed and direction of the migration of both gold and silver sols prepared by electrical dispersion when aluminum sulphate was added to the solution. From his previous work[1] in the preparation of colloidal dispersions of gold, silver, platinum, copper, iron and other metals he concluded that "the formation of colloidal solutions is due to a chemical reaction between the metal and the solvent" (p. 426). To prepare his gold sols he used water which he claims had a specific conductivity of about 1.3×10^{-6} mhos., and without adding any electrolyte he arced gold electrodes in it until he obtained sols of the desired concentration. The specific conductivity of the resulting solutions varied between 3.6 and 10.5×10^{-6} mhos., which is a much larger increase than that found by Beans and Eastlock[2]. On repeating this work in the present investigation using water with a specific conductivity between 0.90 and 1.8×10^{-6} mhos. it was found that the conductivity of the resulting solution increased with the time of arcing (see table I). In all cases it was found that the sols were colored blue and were unstable, precipitating after standing from three minutes to two hours. The more concentrated sols precipitated the most rapidly. These results lead to the conclusion that Burton probably had some impurity present which stabilized his sols. Using sols prepared in this way, he found that by the gradual addition of a 0.001N aluminum sulphate solution the migration velocity of the gold sol decreased and finally reversed its direction. He concludes from this data that a gold sol can be either a positive or negative sol and still be stable. This result contradicts the work of Beans and Eastlack, who found that both in acid and alkaline solutions the gold particles had a negative charge. Since it was not possible to prepare stable sols in pure water, sols containing about 100 mg. of gold per liter were prepared in 0.00005N hydro-

[1]Phil. Mag. 12, 472 (1906).
[1]Phil. Mag. 11, 440 (1906).
[2]Loc. cit., p. 2675.

chloric acid and in 0.0001N sodium hydroxide solutions, using the form of apparatus described previously. By adding freshly prepared 0.001N aluminum sulphate to these solutions and determining the direction but not the speed of migration in a U tube, it was found that when the aluminum ion was added in slight excess of that required (according to Burton's data) to neutralize the charge on the gold particles the sol turned blue and the particles no longer migrated with the current, but collected in the bottom of the tube. On repeating this experiment with an aluminum sulphate solution which had been boiled a short time or to which a trace of ammonium hydroxide had been added followed by dialysis, the sols again changed from red to blue. But in these sols the blue gold particles did migrate to the negative pole. These results give a possible explanation of Burton's reversal of charge of gold sols as being due to the positively charged aluminum hydroxide sol which absorbed the gold particle and carried it to the cathode. Zsigmondoy[1] has shown that aluminum hydroxide sol absorbs gold particles from a colloidal gold dispersion and forms a red colored lake. He also found that the gold absorbed by the aluminum hydroxide sol was protected against the addition of salt just the same as that which is combined with gelatin. The greater stability of Burton's solutions with the larger amount of aluminum solution present probably was due to the presence of the positive aluminum hydroxide sol which Zsigmondy found acted as a protective colloid for gold. In the experiments reported above the concentration of the colloidal aluminum hydroxide was very small compared to the concentration of aluminum ion (which has a high precipitating value) which would account for the precipitation of the gold sol before any noticeable adsorption took place by the small amount of aluminum hydroxide sol present. Since in Burton's work some of the aluminum probably was present as aluminum hydroxide sol and not as aluminum ion, it is quite evident that Lewis' computation[1] of the charge on a colloidal gold particle as being 200 times as large as the charge on the aluminum ions is incorrect.

[1]Zur Erkenntnis der Kolloide, p. 119 (1905).

Experimental.

The following 5 tables show the change in the specific conductivity of different solutions due to arcing:

TABLE I.

Conductivity Water.

Time of arcing in 50 c.c.	Original solution	K x 10^{-6} mhos. after arcing	Difference
1 minute	0.866	1.770	+0.914
	1.290	1.750	+0.460
	0.973	1.330	+0.367
2 minutes	0.950	2.460	+1.510
3 minutes	1.820	4.710	+3.890
	0.904	3.920	+3.016
5 minutes	1.138	7.367	+6.230

TABLE II.

0.002N H_2SO_4

Date	Original solution	K x 10^{-6} mhos. Arced 5 min. in 500 c.c.	Difference
6/30/20	771.3	772.7	+1.40
7/1/20	771.3	772.7	+1.40
7/7/20	771.8	773.4	+1.60
7/9/20	770.8	773.1	+2.30
7/12/20	770.5	771.8	+1.30

TABLE III.

0.00005N HC1

Date	Original solution	K x 10^{-6} mhos. 500 c.c. arced 5 min.	500 c.c. arced 10 min.
5/14/20	19.87	20.35	23.73
5/20/20	20.62	20.10	23.95
5/21/20	19.87	19.96	24.28
5/26/20	20.52	19.84	24.48
5/27/20	20.56	19.84	25.53
6/1/20	20.11	20.75	23.33
Average	20.25	20.14	23.71
Difference	....	−00.11	+03.46
Gold in solution		0.0155 grs.	0.02610 grs.
Gold settled out in 17 days ...		0.0141 grs.	0.0299 grs.

TABLE IV.

0.001N HC1.

Date	Original solution	K x 10-6 mhos. 500 c.c. arced 5 min.	500 c.c. arced 10 min.
6/2/20	425.8	421.4	421.7
6/3/20	425.8	423.6	424.9
6/4/20	425.6	425.1	426.2
6/9/20	426.3	425.4	426.5
6/17/20	426.3	426.0	427.3
6/22/20	426.5	426.2	427.4
6/25/20	426.8	426.5	427.3
Average	426.1	424.9	425.5
Difference	....	–1.2	–0.6
Gold in solution		0.0204 grs.	0.0368 grs.
Gold settled out in 23 days		0.0128 grs.	0.0326 grs.

TABLE V.

0.001N KC1

Date	Original solution	K x 10-6 mhos. 500 c.c. arced 5 min.	500 c.c. arced 10 min.
4/26/20	149.9	151.1	149.6
4/27/20	149.7	148.6	149.3
4/28/20	149.4	149.4	149.3
4/30/20	149.3	149.3	149.3
5/3/20	149.7	149.2	149.3
5/7/20	149.5	149.3	149.3
5/10/20	149.6	149.2	149.4
Average	149.6	149.4	149.4
Difference	....	–0.2	–0.2
Gold in solution		0.0158 grs.	0.0267 grs.

The sols prepared in 0.001N hydrochloric acid, 0.0005N hydrochloric acid, and 0.001N potassium chloride were stable while the sols in conductivity water and 0.002N sulphuric acid precipitated completely. Since the change in the specific conductivity of these solutions is very small, and since in conductivity water the difference increased with the time of arcing, the effect of longer arcing on other solutions was investigated. Whitney and Blake[1] mention a gold sol which contained "several grams of gold per liter," and as the most concen-

[1]Loc. cit., p. 1350.

trated sol recorded above contained only 100 mg. per liter, a sol as concentrated as the one mentioned by Whitney and Blake ought to show a very large change in conductivity. To prepare concentrated sols, the solutions were placed in a pyrex beaker and surrounded by ice and vigorously stirred during arcing with a glass stirred connected to a small motor. The temperature was thus maintained between 20° and 25° C. The turbid looking sols were then placed in well-steamed glass tubes and centrifuged for one hour in a centrifuge which developed a force about 1200 times gravity. After centrifuging, the solutions were clear both by transmitted and reflected light, and all the coarse particles had collected in the bottom of the tubes. In order to prove that centrifuging for one hour resulted in a sol of constant gold content, the following experiment was performed: 100 c. c. of 0.001N, hydrochloric acid, was arced for 10 minutes, one-half of this solution after centrifuging for 30 minutes gave 0.0635 grs. of gold per liter; the other half after centrifuging for one hour gave 0.0652 grs. of gold per liter. The red clear upper layer was siphoned off, precipitated with a few drops of hydrochloric acid, filtered through an ashless filter paper, burned and weighed in a porcelain crucible. The filtrate was tested for gold by means of an alkaline solution of hydrogen peroxide[1], which quantitatively precipitates the gold in concentrations as low as 0.03 mg. in 10 c.c., and in all cases this test failed to show the presence of any gold. The amount of solution used in each determination was sufficient to give 50 mg. of gold. Following are the results obtained with 0.00005N, hydrochloric acid.

Time of arcing for 1 liter	Grams of gold per liter	Time of arcing for 1 liter	Grams of gold per liter
80 minutes	0.3093	300	0.6460
100 minutes	0.3546	350	0.6963
140 minutes	0.4662	400	0.6018
170 minutes	0.5270	440	0.8258
240 minutes	0.5771	460	Sol precipitated
		500	Sol precipitated before arcing was finished

It was found that 0.0002N. hydrochloric acid precipitated in about 400 minutes; 0.002N hydrochloric acid precipitated in about 200 minutes; 0.005N sodium hydroxide in about 150 minutes; and 0.002N sodium hydroxide in about 180 minutes

[1]Vanino and Seeman-Ber. 32, 1968 (1899).

of arcing. With 0.001N potassium iodide the saturation point was 0.0263 grs. per liter, and with 0.001N sodium bromide it was 0.7390 grs. per liter, thus showing that the amount of gold which passes into the colloidal condition in the chloride, bromide, and iodide solutions is in the order of the stability of the compounds formed by gold with these anions. From these data it is seen that the maximum concentration of gold that can be obtained by this method is about 825 mgrs. per liter. Because of the fact that long-continued arcing precipitates the sol, it was thought best to use sols containing between 0.400 grs. and 0.500 grs. of gold per liter for conductivity titration analysis. These solds were very stable and gave very noticeable changes in conductivity.

Method of Procedure

The titration curves were made at 25° ± .003C. using a small Freas conductivity cell of 50 c. c. capacity, taking 25 c. c. aliquots of the solutions to be titrated and allowing 20 minutes for them to attain the temperature of the bath. The titrating solution was 10 times the concentration of the solution to be titrated, and was measured out by a calibrated microburette of 1 c. c. capacity and graduated in hundredths of a cubic centimeter. This titrating solution was kept in the thermostat between measurements, and so only five minutes was allowed for the solution in the cell to come to temperature after each addition. All titrations were made in duplicate, using aliquots from the original solution and from the sol. For the freezing experiments, 30 c. c. portions were pipetted into a thoroughly steamed and dried flask, which was then carefully sealed with a rubber stopper. The flask was then surrounded by a mixutre of ice and salt until the solution had frozen solid. The ice was melted and the solution allowed to come to temperature in the thermostat, after which 25 c. c. of the solution was pipetted into the conductivity cell and the conductivity titration curve determined in the same manner as described above. For measuring the effect of the precipitation of the sols by centrifuging 30 c. c. portions were placed in the gold-plated inner bowl of a Sharples Laboratory super-centrifuge after it had been thoroughly steamed out. Three minutes centrifuging at 35,000 r. p. m. equivalent to a force 32,000 times gravity was sufficient to throw out every gold sol prepared in pure solutions. The precipitate was black, and adhered so strongly to

the bowl that it could not be again dispersed by shaking with water. After centrifuging the sols, 25 c. c. of the clear liquid was pipetted in a conductivity cell and the conductivity titration curve determined as described above.

The neutral point was found by prolonging the two straight arms of the titration curves until they intersected. This method was used by Dutoit[1] and by Kolthoff[2], who found it to give correct results. On the assumption that the conductivity of ions is an additative property the above curves ought to give two straight lines which intersect at the neutral point. The $AgN0_3$-HC1 curves very closely approximate this condition; the 0.001N HC1-0.01N NaOH curves deviate slightly from the theoretical; and the 0.001N Na0H-0.01N HC1 curves show a larger deviation. The flat portions in the curves are probably due to the presence of carbonate, since freshly prepared solutions of acid and base gave curves which very closely approached the theoretical. If an equal volume of 0.01N sodium carbonate is added to 0.01N sodium hydroxide and 0.001N hydrochloric acid titrated with this mixture, the curve has a very much wider flat point than when sodium hydroxide is used alone, but the neutral point is the same in both cases.

Following are the data obtained as outlined above:

TABLE VI.

0.001N Na0H titrated with 0.01N HC1

Original solution.		Sol (0.1264 grs. gold per 1)	
c.c. of acid added	K x 10^4 mhos.	c.c. of acid added	K x 10^4 mhos.
0.00	2.114	0.00	1.725
0.40	1.880	0.40	1.539
0.80	1.657	0.80	1.390
1.00	1.550	1.20	1.275
1.20	1.454	1.40	1.238
1.60	1.288	1.60	1.215
1.80	1.227	1.80	1.211
2.00	1.192	2.00	1.234
2.20	1.210	2.20	1.255
2.40	1.238	2.40	1.278
2.60	1.455	2.60	1.321
2.80	1.759	2.80	1.536
Neutral point = 2.23 c.c.		Neutral point = 2.15 c.c.	

[1]Loc. cit.
[2]Loc. cit.

TABLE VII.

0.005N NaOH titrated with 0.05N HCl

Original solution		Sol (0.3021 grs. gold per liter)		Sol after centrifuging	
c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.
0.00	11.93	0.00	9.532	0.00	8.083
0.30	10.96	0.20	8.976	0.40	7.034
0.60	10.02	0.40	8.455	0.80	6.124
0.90	9.128	0.60	7.963	1.20	5.474
1.20	8.258	0.80	7.452	1.40	5.294
1.50	7.411	1.00	6.959	1.70	5.186
1.80	6.623	1.20	6.509	2.00	5.288
2.10	6.046	1.50	5.876	2.20	5.378
2.40	6.103	1.80	5.454	2.50	6.685
2.60	7.640	2.10	5.346	2.70	8.021
2.70	8.459	2.30	5.433	2.90	9.380
2.80	9.255	2.50	5.546	3.00	10.09
		2.70	6.659		
Neutral pt. = 2.29 c.c.		2.90	7.998	Neutral pt. = 2.07 c.c.	
		3.00	8.662		
		Neutral pt. = 2.26 c.c.			

TABLE VIII.

0.002N NaOH titrated with 0.02N HCl

Original solution		Sol (0.4268 grs. gold per liter)		Sol after freezing	
c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.
0.00	4.707	0.00	3.566	0.00	3.298
0.50	4.144	0.50	3.094	0.40	2.911
1.00	3.611	1.00	2.717	0.80	2,625
1.50	3.103	1.50	2.482	1.20	2.442
1.80	2.815	1.80	2.429	1.50	2.372
2.00	2.645	2.00	2.433	1.80	2.377
2.20	2.500	2.20	2.473	2.00	2.409
2.40	2.409	2.40	2.513	2.40	2.486
2.60	2.449	2.60	2.549	2.80	2.632
2.80	2.869	2.80	2.608	3.00	2.915
3.00	3.427	3.20	3.100	3.20	3.133
Neutral pt. = 2.50 c.c.		Neutral pt. = 2.02 c.c. (sol precipitated during titration)		Neutral pt. = 1.99 c.c.	

Original solution		Sol (0.4268 grs. gold per 1)	
c.c. of acid added	K x 10^4 mhos.	c.c. of acid added	K x 10^4 mhos.
0.00	4.640	0.00	3.397
0.50	4.060	0.40	3.026
1.00	3.522	0.90	2.654
1.50	3.014	1.20	2.505
1.80	2.739	1.50	2.418
2.20	2.453	1.80	2.400
2.40	2.388	2.20	2.464
2.60	2.434	2.60	2.540
2.80	2.843	2.80	2.610
3.00	3.414	3.00	2.774
3.20	3.537	3.20	2.998
Neutral pt. = 2.49 c.c.		Neutral pt. = 2.05 c.c. (sol precipitated during titration)	

TABLE IX (Figure I)

0.001N NaOH titrated with 0.01N HCl

Original solution		Sol (0.3852 grs. gold per liter)		Sol after freezing	
c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.
0.00	1.905	0.00	1.381	0.00	1.247
0.30	1.742	0.20	1.315	0.20	1.993
0.60	1.575	0.40	1.263	0.40	1.152
0.90	1.438	0.60	1.233	0.60	1.123
1.20	1.322	0.90	1.181	0.90	1.127
1.50	1.234	1.20	1.182	1.20	1.160
1.80	1.203	1.50	1.212	1.50	1.190
2.10	1.234	1.80	1.240	1.80	1.224
2.40	1.289	2.20	1.280	2.20	1.322
2.60	1.542	2.40	1.314	2.40	1.759
2.80	1.844	2.60	1.402	2.60	1.844
		2.80	1.581	2.70	1.998
Neutral pt. = 2.08 c.c. (Curve A)		Neutral pt. = 1.93 c.c. (Curve B)		Neutral pt. = 1.89 c.c. (Curve C)	

c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.	c.c. acid added	K x 10^4 mhos.
0.00	1.784	0.00	1.351	0.00	1.123
0.30	1.631	0.20	1.291	0.20	1.104
0.70	1.448	0.40	1.244	0.40	1.114
0.90	1.370	0.60	1.208	0.60	1.132
1.20	1.268	0.80	1.189	0.80	1.153
1.50	1.195	1.00	1.176	1.00	1.174
1.80	1.195	1.40	1.193	1.40	1.218
2.00	1.214	1.80	1.226	1.80	1.269
2.20	1.237	2.20	1.261	2.20	1.519
2.40	1.271	2.40	1.286	2.40	1.794
2.60	1.484	2.60	1.352		
2.80	1.782	2.80	1.518		
Neutral pt. = 2.10 c.c. (Curve A')		Neutral pt. = 1.95 c.c (Curve B')		Neutral pt. = 1.80 c.c. (Curve C')	

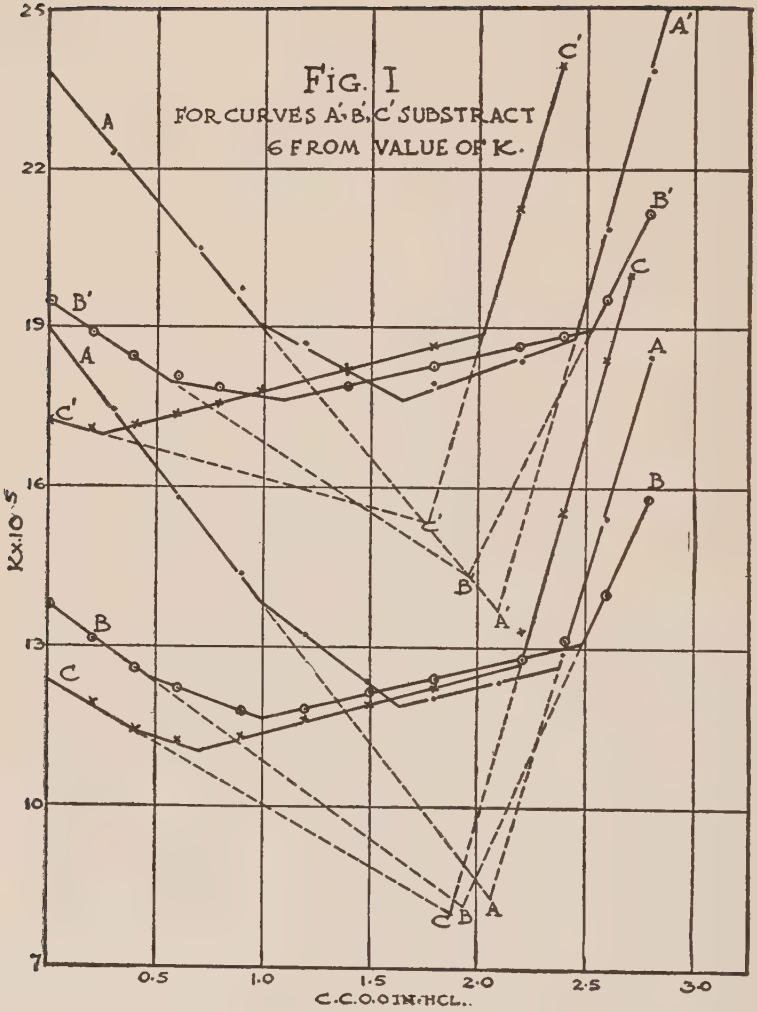
FIG. I
FOR CURVES A', B', C' SUBSTRACT
6 FROM VALUE OF K.
K x 10⁻⁵
C.C. 0.01 N. HCL.
25
22
19
16
13
10
7
0.5
1.0
1.5
2.0
2.5
3.0
A
B
C
A'
B'
C'

TABLE X (Figure II)

0.001N HCl titrated with 0.01N NaOH

Original solution		Sol (0.4079 grs. gold per liter)		Sol after freezing	
c.c. NaOH added	K x 10^4 mhos.	c.c. NaOH added	K x 10^4 mhos.	c.c NaOH added	K x 10^4 mhos.
0.00	4.239	0.00	3.959	0.00	4.145
0.40	3.661	0.40	3.416	0.40	3.567
0.80	3.114	0.80	2.886	1.00	2.799
1.20	2.593	1.20	2.370	1.50	2.209
1.60	2.086	1.60	1.887	2.00	1.510
2.00	1.592	2.00	1.432	2.20	1.315
2.20	1.357	2.20	1.234	2.40	1.312
2.40	1.236	2.40	1.231	2.60	1.362
2.60	1.287	2.60	1.282	2.80	1.460
2.80	1.419	2.80	1.366	3.00	1.593
3.00	1.553	3.00	1.486	3.20	1.755
Neutral pt. = 2.30 c.c. (Curve A)		Neutral pt. = 2.23 c.c. (Curve B)		Neutral pt. = 2.28 c.c. (Curve C)	

				Sol after centrifuging	
c.c. NaOH added	K x 10^4 mhos.	c.c. NaOH added	K x 10^4 mhos.	c.c NaOH added	K x 10^4 mhos.
0.00	4.201	0.00	4.100	0.00	1.243
0.50	3.490	0.50	3.402	0.20	1.189
1.00	2.808	1.00	2.737	0.40	1.182
1.50	2.158	1.50	2.108	0.70	1.164
1.80	1.780	1.80	1.743	1.00	1.151
2.00	1.537	2.00	1.516	1.40	1.142
2.20	1.303	2.20	1.295	1.80	1.148
2.40	1.254	2.40	1.261	2.20	1.234
2.60	1.315	2.60	1.326	2.40	1.362
2.80	1.431	2.80	1.393	2.70	1.591
3.00	1.564	3.00	1.496	3.00	1.824
3.20	1.704	3.20	1.616		
Neutral pt. = 2.28 c.c. (Curve A′)		Neutral pt. = 2.25 c.c. (Curve B′)		Neutral pt. = 1.58 c.c. (Curve C′)	

				Sol after centrifuging.	
0.00	4.224	0.00	4.103	0.00	1.208
0.50	3.521	0.50	3.414	0.20	1.140
1.00	2.839	1.00	2.758	0.30	1.136
1.50	2.185	1.50	2.124	0.40	1.154
1.80	1.803	1.80	1.762	1.00	1.105
2.00	1.557	2.00	1.536	1.50	1.092
2.20	1.315	2.20	1.317	1.80	1.108
2.40	1.252	2.40	1.281	2.20	1.212
2.60	1.310	2.60	1.332	2.40	1.344
2.80	1.420	2.80	1.393	2.60	1.486
3.00	1.550	3.00	1.491	2.80	1.632
3.20	1.688	3.20	1.614	3.00	1.778
Neutral pt. = 2.29 c.c.		Neutral pt. = 2.26 c.c.		Neutral pt. = 1.58 c.c.	

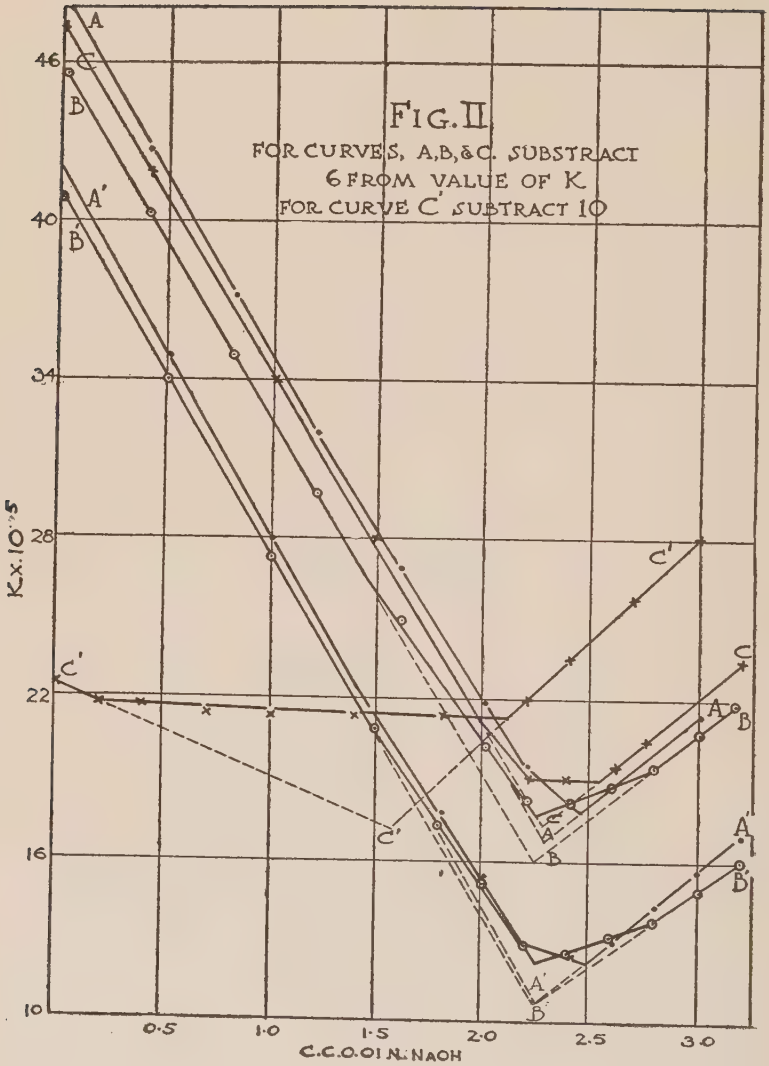
FIG. II
FOR CURVES, A,B,&C. SUBSTRACT
6 FROM VALUE OF K
FOR CURVE C' SUBTRACT 10
K.X.10^5
C.C.0.01 N. NaOH
46
40
34
28
22
16
10
0.5
1.0
1.5
2.0
2.5
3.0
A
C
B
A'
B'
C'

TABLE XI.

0.002N HC1 titrated with 0.02N NaOH

Original solution		Sol (0.5270 grs. gold per liter)	
c.c. NaOH added	K x 10^4	c.c. NaOH added	K x 10^4
0.00	8.397	0.00	7.231
0.50	7.004	0.50	5.936
1.00	5.682	1.00	4.757
1.50	4.394	1.50	3.579
2.00	3.193	2.00	2.529
2.30	2.496	2.30	2.362
2.60	2.482	2.60	2.492
2.80	2.764	2.80	2.742
3.00	3.026	3.00	3.022
Neutral pt. = 2.40 c.c.		Neutral pt. = 2.23 c.c. (Sol precipitated during titration)	

TABLE XII (Figure III)

0.001N HCl titrated with 0.0095N $AgNO_3$

Original solution		Sol (0.4079 grs.)		Sol after centrifuging	
c.c. $AgNO_3$ added	K x 10^4 mhos.	c.c. $AgNO_3$ added	K x 10^4 mhos.	c.c. $AgNO_3$ added	K x 10^4 mhos.
0.00	4.182	0.00	4.099	0.00	1.244
0.50	4.107	0.50	4.024	0.40	1.223
1.00	4.025	1.00	3.946	0.80	1.196
1.50	3.941	1.50	3.873	1.20	1.180
2.00	3.864	2.00	3.807	1.60	1.153
2.40	3.803	2.40	3.784	2.00	1.140
2.60	3.779	2.60	3.850	2.40	1.275
2.80	3.797	2.80	3.928	2.80	1.444
3.00	3.856	3.00	4.012	3.00	1.526
3.40	3.974	3.40	4.162	Neutral pt. = 2.06 c.c.	
3.80	4.091	3.80	4.401	(Curve C)	
Neutral pt. = 2.68 c.c. (Curve A)		Neutral pt. = 2.34 c.c. (Curve B)			
		(approximately 0.8569 grs. per liter)		(approx. 0.850 grs. per liter)	
0.00	4.266	0.00	4.276	0.00	3.175
0.40	4.192	0.40	4.448	0.40	3.306
0.80	4.133	0.80	4.542	0.80	3.321
1.20	4.074	1.20	4.543	1.20	3.321
1.60	4.016	1.60	4.550	1.60	3.340
2.00	3.952	2.00	4.543	2.00	3.332
2.40	3.891	2.40	4.528	2.40	3.335
2.60	3.868	2.80	4.639	2.80	3.455
2.80	3.880	3.20	5.155	3.20	4.194
3.40	4.049	Neutral pt. = 0.00 c.c.		Neutral pt. = 0.00 c.c.	
3.80	4.166	(Curve B′)		(Curve B″)	
		(sol precipitated during titration)		(sol precipitated during titration)	
Neutral pt. = 2.70 c.c. (Curve A′)					

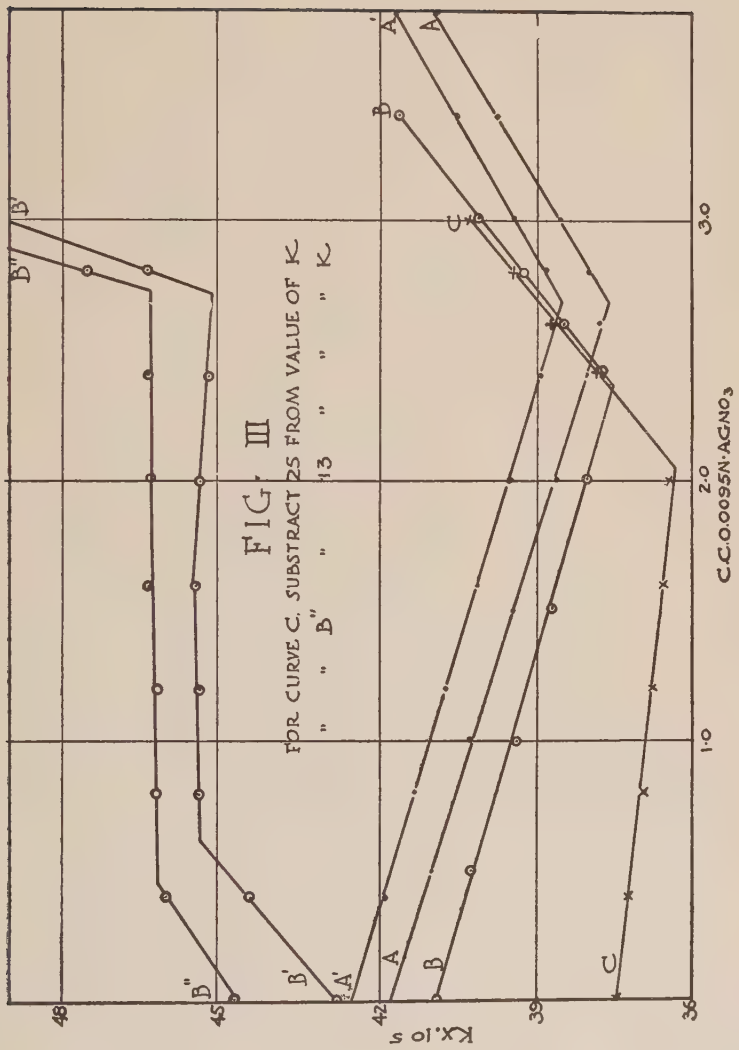
FIG. III
FOR CURVE C. SUBSTRACT 25 FROM VALUE OF K
" " B" " 13 " " " K
K.10 5
C.C.0.0095N.AGNO3
1.0
2.0
3.0
36
39
42
45
48
A
B
C
A'
B'
B"

TABLE XIII (Figure IV)

0.0011NHO titrated with .0095N $AgNO_3$

A

Original solution		Sol (0.1848 grs. gold per liter)		Sol. after centrifuging	
c.c. $AgNO_3$ added	K x 10^4 mhos.	c.c. $AgNO_3$ added	K x 10^4 mhos.	c.c. $AgNO_3$ added	K x 10^4 mhos.
0.00	4.451	0.00	4.442	0.00	1.559
0.50	4.352	0.50	4.381	0.50	1.529
1.00	4.259	1.00	4.302	1.00	1.500
1.50	4.175	1.50	4.236	1.50	1.470
2.00	4.039	2.00	4.160	2.00	1.439
2.50	4.015	2.40	4.111	2.40	1.422
2.80	3.972	2.60	4.092	2.60	1.424
3.00	3.993	2.80	4.076	2.80	1.486
3.20	4.044	3.00	4.111	3.00	1.564
3.60	4.156	3.40	4.237	3.20	1.640
4.00	4.259	3.80	4.358	3.40	1.716
Neutral pt. = 2.86 c.c. (Curve A)		Neutral pt. = 2.80 c.c. (Curve B)		Neutral pt. = 2.60 c.c. (Curve C)	

B

Sol (0.381 grs.)		Sol after freezing		Sol after centrifuging	
0.00	4.397	0.00	4.536	0.00	1.472
0.50	4.369	0.50	4.401	0.50	1.482
1.00	4.325	1.00	4.342	1.00	1.455
1.50	4.272	1.50	4.245	1.50	1.435
2.00	4.217	2.00	4.164	2.00	1.424
2.50	4.169	2.50	4.069	2.20	1.423
2.60	4.177	2.70	4.052	2.40	1.472
3.00	4.233	3.00	4.120	2.60	1.555
3.40	4.364	3.40	4.235	2.80	1.640
3.80	4.478	3.80	4.332	3.00	1.719
Neutral pt. = 2.71 c.c. (Curve A′)		Neutral pt. = 2.67 c.c. (Curve B′)		Neutral pt. = 2.24 c.c. (Curve C′)	

C

Sol (0.8330 grs.)		Sol after centrifuging	
0.00	4.029	0.00	1.869
0.50	4.005	0.50	1.823
1.00	3.941	1.00	1.783
1.50	3.904	1.50	1.746
2.00	3.890	1.80	1.727
2.40	3.960	2.00	1.715
2.60	4.042	2.20	1.738
2.80	4.159	2.40	1.816
3.00	4.254	2.80	1.962
Neutral pt. = 2.24 c.c. (sol precipitated during titration) (Curve A″)		3.00	2.027
		Neutral pt. = 2.08 c.c. (Curve C″)	

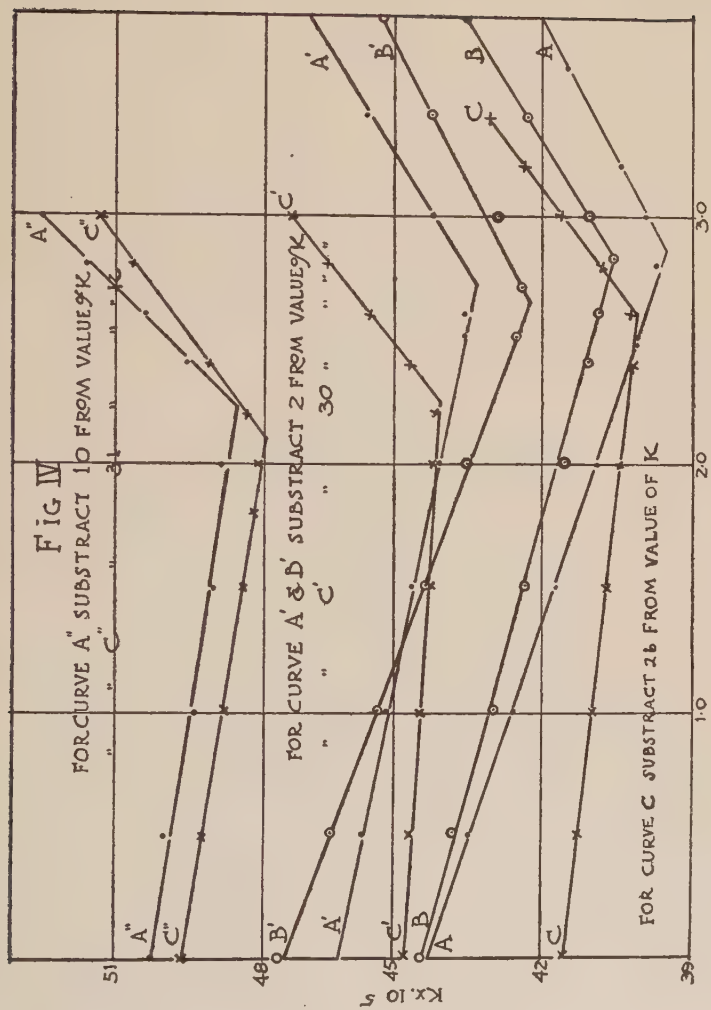
Fig IV
FOR CURVE A" SUBSTRACT 10 FROM VALUE OF K
" " C" " 21 " " " "
" " C' " 30 " " " "
FOR CURVE A' & B' SUBSTRACT 2 FROM VALUE OF K
FOR CURVE C SUBSTRACT 26 FROM VALUE OF K
C.C.O. 0086 N. AgNO3
K x 10 5
51
48
45
42
39
1·0
2·0
3·0
A"
C"
B'
A'
C'
B
A
C

SUMMARY OF DATA FROM TITRATION CURVES

Table XIV.

Conc. of Solutoin to be titrated		Conc. of titrating solution	Mg. of negative ion per mg. gold	Neutral point of Original solution	Neutral point of Sol	Sol after freezing	Sol after centrifuging	Data found in table
0.001N	NaOH	O.001HCl	0.00431	2.23	2.15	.....	.....	VI
0.005N	NaOH	0.05NHCl	0.00337	2.29	2.26	.....	2.07	VII
0.002N	NaOH	0.02NHCl	.....	2.50	2.02	1.99	.....	VIII
			.....	2.49	2.05	.....	.....	
0.0C1N	NaOH	0.01NHCl	0.00300	2.08	1.93	1.89	.....	IX
			0.00300	2.10	1.95	.....	1.80	
0.001N	HCl	0.01NNaOH	.....	2.30	2.23	2.28	.....	X
			.....	2.28	2.25	.....	1.58	
			.....	2.29	2.26	.....	1.58	
0.002N	HCl	0.02NNaOH	.....	2.40	2.23	.....	.....	XI
0.001N	HCl	0.0095N $AgNO_3$	0.01110	2.68	2.34	.....	2.06	XII
			.....	2.70	0.00	.....	.....	
			.....	.....	0.00	.....	.....	
0.0011N	HCl	0.0095N $AgNO_3$	0.00460	2.86	2.80	.....	2.60	XIII
			0.00560	.....	2.71	2.67	2.24	
			0.C1060	.....	2.24	.....	2.08	

The summary of the data from the titration curves shows that the negative ions of the solutions tested had a lower concentration in the gold sols than they had in the solutions from which the sols were made. The difference between the two concentrations is greater in concentrated sols than it is in dilute sols. On the other hand the concentration of the hydrogen ion is the same in all stable gold sols as it is in the original solution. In the data given in Table XI, where the sol precipitated before the titration was finished, there is adsorption of hydrogen ion. That the decreased concentration of the negative ions in stable sols is not due to adsorption but to the formation of a complex with the gold particles similar to a chemical combination is shown by several facts. In the first place the large decrease in the hydroxyl ion concentration shown in Table VIII is partly due to adsorption and partly due to some other factor because in these solutions the sols precipitated before the titration was finished. The difference of 0.48 and 0.45 c.c. of 0.02N hydrochloric acid in the neutral points is

very much larger than it is for any other stable sol with approximately the same concentration of gold. This difference is the sum of the effect of adsorption and of complex formation. In the second place it has been shown by Whitney and Blake[1] that long-continued dialysis will separate only a certain amount of the ions from the sols, but not all of them. In the third place Beans and Eastlack have shown that the stability of the sol depends upon the presence of certain negative ions in concentrations between 0.005N and 0.00005N. The migration experiments (page 7) also show that stable sols depend upon the presence of electrolytes in concentrations above 0.00001N. In the fourth place the precipitation of the sols by freezing shows that the electrolyte is combined with the gold in a different manner than by adsorption because all the data given by the titration curves shows that the neutral point for both positive and negative ions was the same (within experimental error) after freezing as it was before. In other words, the concentration of both ions was the same after precipitation of the sol by freezing as it was in the stable sol, which fact shows that the precipitation was not due to a change in concentration of ions but to a change in their relationship to the gold. The experiments with the Sharples super-centrifuge show that precipitation of the sol by mechanical means (without altering the concentration of the electrolyte present) causes it to adsorb both positive and negatvie ions from the solution. In this case the complex as a whole was thrown out, carrying with it some adsorbed ions. This behavior is in accord with the way the sols in Tables VIII and XI acted since they showed a decrease in both positive and negative ions due to precipitation of the sol. But since in freezing there was no noticeable adsorption of either ion, we may conclude that this was due to the fact that the complex was destroyed and that gold particles as such adsorb very little electrolyte.

It is interesting to note in this connection that a sol precipitated by mechanical means, as for example by centrifuging, is not reversible, or in other words the precipitate cannot be again dispersed by shaking with water or a solution containing electrolyte. However, such reversibility is produced by addition of small quantities of protective colloids such as gelatin. To illustrate this property the following experiment may be cited. After adding 5 c.c. of a 0.1% gelatin solution to

[1]Loc. cit.

50 c.c. of a gold sol it required 16 min. centrifuging at 35,000 r.p.m. to throw out all the gold. The precipitated gold in this case was red in color and could be dispersed by shaking with water, forming a stable red sol. On heating some of the precipitate in a crucible it showed a slight charring, which indicates the presence of gelatin with the gold. The same concentration of a pure gelatin solution showed no precipitation of the gelatin even after 30 min. of centrifuging. These results can be explained on the assumption that the gelatin adsorbed by the gold was thrown out of solution along with the gold, while the unadsorbed gelatin remained in solution.

Comparing Tables VI, IX, XII, and XIII it is seen that the amount of electrolyte taken out of solution increases with increase in the concentration of gold in the dispersed condition, although this relationship is not strictly quantitative. These variations are due to several causes, among which may be mentioned the difference in the size of the gold particles (the smaller particles having the largest effect), the different concentration of the electrolytes, the effect of packing the gold particles closer together, and the effect of the arc on the decomposition of the solution (very noticeable when arcing in conductivity water). Since there is a relationship between the amount of gold in a colloidal dispersion and the amount of electrolyte required to stabilize the sol, it follows that the hydroxyl ion concentration of conductivity water ought to stabilize a small amount of gold. The cause of the absence of even traces of stable colloidal gold in conductivity water is explained by observing the effect of arcing in a solution of a 0.00005N, hydrochloric acid, sol, which has been diluted until the concentration of electrolyte was 0.0000005N. According to Zzsigmondy[1], the presence of a small amount of colloidal gold in a solution of gold chloride while it is being reduced by formaldehyde will affect the size of the particles of gold formed because the small gold particles act as nuclei. Therefore the 0.0000005N hydrochloric acid sol which was prepared by dilution four months previously, and had shown no evidence of instability, ought to furnish sufficient nuclei to act as condensation centers for the formation of a stable sol. It was found, however, that arcing in such a solution always formed a blue sol which precipitated slowly or rapidly, depending on the length of time of arcing, the longer arcing precipitating the sol the most rap-

[1]Z. Phy. Chem. 56, 65 (1906).

idly. This shows that arcing in such a dilute solution causes all the gold to precipitate, even though the sol before arcing was stable. It is highly probable that the small amount of stable gold that could be formed by arcing in conductivity water would be precipitated in the same way this stable sol was precipitated.

Figure III curves B′ and B″ (Table XII) show the effect of arcing in a 0.001N hydrochloric acid solution until it has reached the saturation point and is almost at the point of precipitating. There appears to be only a minute amount of free chloride ion in solution, since with the first addition of silver nitrate the conductivity increases. Only after a certain amount of silver ion has been added to the solution is the solubility product of silver chloride exceeded, and it begins to precipitate. The conductivity remains constant during further additions of silver nitrate due to the precipitation both of the sol and of silver chloride until the neutral point of the original solution is reached, when it increases very rapidly. Apparently the sol acts as a buffer solution, keeping the concentration of chloride ion very small. As soon as the sol is completely precipitated the conductivity increases very rapidly, thus showing that the chloride ion has also been completely precipitated.

The charge on a gold particle was calculated from the following data: (1) the amount of chloride or hydroxyl ions combined with 1 mg. of gold as given in Table XIV; (2) Avogadro's number was taken as 6.06×10^{23}; (3) the value of the charge on a univalent ion is 3×10^{-10} e.s.u.; (4) the average size of a gold particle was assumed to be 5×10^{-7} c.c. The values calculated for the hydroxyl ion were as follows:

4.5
2.8
3.5
—

Average 3.6×10^{-7} e.s.u.

for the chloride ion:

5:7
2.4
2.9
5.4
—

Average 4.1×10^{-7} e.s.u.

The average of both ions was 3.85 x 10^{-7} e.s.u. The value for the size of the gold particle was assumed to be 5 x 10^{-7} c.m. because gold sols which have been filtered through hardened filter paper or centrifuged until all the coarse particles have settled show very few particles in the ultramicroscope when using a carbon arc as a source of light. With a very strong beam of light particles 5 x 10^{-7} c.m. in size can be seen, while with a source of light such as a carbon arc particles of this size are not readily visible. Therefore since these sols had very few particles visible in the ultramicroscope the calculations will be more nearly correct by assuming the average size to be 5 x 10^{-7} c.m. rather than to take the value 4 x 10^{-5} c.m. as given by Burton.[1] While this calculation only gives us an approximation as to the exact charge on each gold particle, it shows a very important relationship, namely, that the charge due to the hydroxyl ion is of the same order as the one due to the chloride ion.

Summary.

It has been shown that:

(1) There is a certain amount of electrolyte necessary to stabilize a gold sol prepared by electrical dispersion.

(2) The amount of electrolyte necessary to stabilize the sol is roughly proportional to the amount of colloidal gold present.

(3) The negative ion is the active constituent in stabilizing the gold in a gold sol.

(4) Freezing a stable gold sol precipitates the gold by destroying the "complex" between the gold and negative ion.

(5) Centrifuging with a force 35,000 times gravity completely precipitates all stable gold sols.

(6) The "complex" is not destroyed by centrifuging.

(7) The "complex" adsorbs both positive and negative ions.

(8) The average charge on a gold particle was calculated to be 3.85 x 10^{-7} e.s.u. This value was obtained by assuming the average size of the particles to be 5 x 10^{-7} c.m.

[1]Phil. Mag. 12, 477 (1906).

Vita.

David J. Beaver was born in Schenectady, New York, on February 23, 1893, and attended the grade and high schools of that city. He received the degree of B.S. from Union College, Schenectady, New York, in June, 1915. He attended the graduate school of Columbia University from September, 1916, to June, 1917, when he received the degree of M.A. From September, 1917, until December, 1918, he was in the Sanitary Corps of the United States Army stationed at the Gas Warfare Experimental Station, Washington, D.C. In February, 1919, he resumed graduate work at Columbia University, being laboratory assistant in Organic Chemistry during the spring and summer sessions of 1919. From July 1, 1919, until June, 1920, he was De Pont Fellow in Chemistry, and from July, 1920, until the present was Assistant in Chemistry.

MAY 3 1925

FEB 15 1928

FEB 29 1928

STANFORD UNIVERSITY LIBRARIES MAY 13 1922

A Study of the Effect of Certain Electrolytes on Stabilizing and Precipitating Gold Sols.

L C

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE IN COLUMBIA UNIVERSITY

BY

DAVID J. BEAVER, B.S., M.A.

NEW YORK CITY

1921

STANFORD UNIVERSITY LIBRARIES WITHDRAWN

The Jackson Press, Kingston
1921

781
72B

UNCLASSED